

(CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.)

A NEW PROOF OF THE FORMULA $d = \frac{.02T^2}{L}$

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The ordinary student of chemistry has a rather vague conception of thermodynamics, and therefore in van't Hoff's¹ demonstration of the relation between the lowering of the freezing-point of a solution (or the rise of the boiling-point) and certain physical constants of the solvents, he does not know why work is equal to

$$\frac{dT N L}{T n},$$

and hence it loses its entire meaning. The following modification of van't Hoff's demonstration has been found of real value with such students.

Let a solution containing n gram-molecule solute in N grams solvent be put into a cylinder provided with a semi-permeable end and with a movable piston. At $T - dT$ the freezing-point of the solution let freeze out a quantity of the solvent that originally contained one gram-molecule solute, viz., $\frac{N}{n}$ grams. If L' be the latent heat of fusion of the solvent at the temperature $T - dT$, there will be evolved $\frac{N}{n} L'$ calories. Separate the solid from the solution and bring the whole to the temperature T , the melting-point of the solvent. To do this a calories must be added. Allow the solvent to melt. If its latent heat of fusion at the temperature T be L , it will absorb $\frac{N}{n} L$ calories. Now bring the liquid solvent into contact with

¹ Zeit. phys. Chem. 1, 496 (1887).

the solution at the semi-permeable membrane with the pressure on the solution equal to the osmotic pressure. Raising the piston under this constant pressure the solvent passes through the diaphragm, mixing with the solution. The work done on the piston is equal to the osmotic pressure P into the volume of the solvent V . As V is the volume that contained one gram-molecule solute $PV = RT$, or if we express R in thermal units, $\text{Work} = PV = 2T$.

Bring the whole to the original temperature $T - dT$, thus coming back to the starting-point. During this last process b calories are evolved. We therefore have $\left(\frac{N}{n} L + a\right)$ calories absorbed and $\left(\frac{N}{n} L' + b\right)$ calories are evolved. The work done must be the difference between these, or as a and b are practically equal, we may consider $2T = \frac{N}{n} (L - L')$. Consider the solvent an ideal liquid that may be supercooled indefinitely, and let the specific heats of both liquid and solid be constants from absolute zero to the normal melting-point T . If one gram of the liquid phase be at absolute zero it will absorb in going to the temperature T'' , $h_l T''$ calories if h_l be its specific heat. In like manner, one gram of the solid will absorb $h_s T''$ calories if h_s be its specific heat. The latent heat of fusion at the temperature T'' will therefore be $(h_l - h_s)T''$, and at any temperature T it will be $(h_l - h_s)T$. Substituting for L and L' in the expression $2T = \frac{N}{n} (L - L')$ their values $(h_l - h_s)T$ and $(h_l - h_s)(T - dT)$, we get $2T = \frac{N}{n} (h_l - h_s)dT$, and substituting for $h_l - h_s$ its value $\frac{L}{T}$, the expression becomes $2T = \frac{N}{n} dT \frac{L}{T}$ or $dT = \frac{2T^2}{L} \cdot \frac{n}{N}$ or for one gram-molecule solute in 100 grams solvent $dT = \frac{.02T^2}{L}$.

Of course we have assumed ideal conditions but they may be considered as realized for very dilute solutions and slight differences of temperature. The corresponding expression for the

rise of the boiling-point may be derived in a similar manner.

A point made clear by this demonstration is that the specific heat of a liquid must be greater than that of its solid or its vapor within the same range of temperature. Otherwise the solution might have a lower boiling-point or a higher freezing-point.